DERWENT-ACC-NO: 1994-171270

DERWENT-WEEK: 199421

TITLE: Prepn. of solid electrolytic capacitor - by forming dielectric oxide film on metal foil, forming polymer film from pyridine soln. and forming electroconductive polymer film there on

PATENT-ASSIGNEE: ELNA KK[ELNA]

PRIORITY-DATA: 1992JP-0280610 (September 25, 1992)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
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APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 06112094A	N/A	1992JP-0280610	September 25, 1992

INT-CL (IPC): C08G061/12, H01G009/02

ABSTRACTED-PUB-NO: JP 06112094A

BASIC-ABSTRACT:

A solid electrolytic capacitor is prepd. by forming dielectric oxide film on valve-acting metal foil, forming polymer film on the oxide film by immersing the metal foil in an electrolytic soln. comprising an aq. monomer soln. and an aq. oxidising agent soln., one of which contains a cpd. contg. pyridine rings and polymerising chemically oxidatively the monomer and polymerising electrolytically electroconductive polymer on the polymer film.

The chemical polymerisation is carried out by immersing valve-acting metal foil (e.g., etched Al foil) in an aq. soln. contg. 5-50 wt.% monomer (e.g., pyrrole, thiophene, furan or aniline) and a solvent (e.g., H2O contg. ethanol, methanol, acetonitrile, propylene carbonate or N,N-DMF in a concn. = 0.1-5.0 mol/l) and then immersing the foil in an aq. soln. of an oxidising agent (e.g., a halogen, metal halide (e.g., AsF5, PCl5, AlCl3, etc.), protonic acid (e.g., H2SO4, HSO3F, etc.), peroxide (e.g., H2O2, peracetic acid, etc.), ferrous salt or cupric salt, etc.) in a concn. = 0.01-5.0 mol/l) together with a supporting electrolyte (e.g., p-toluene-, naphthalene- or benzene -sulphonic acid, benzoic adipic, oxalic or phthalic acid, naphthylphosphoric acid or phenylboric acid)

to polymerise the monomer in the pores and on the surface of the foil. A cpd. contg. pyridine ring (e.g., pyridine, pyridazine, 2(3-pyridyl)pyrrole or 2,3'-bipyridine) is used in the aq. monomer soln. or in the aq. oxidising agent soln. together with a supporting electrolyte.

ADVANTAGE - The pyridine ring-contg. cpd. added into the aq. monomer soln. or the aq. oxidising agent soln. reduces the specific resistivity to reduce the equiv. series resistance and to improve the impedance of the capacitor.

CHOSEN-DRAWING: Dwg.0/1

TITLE-TERMS: PREPARATION SOLID ELECTROLYTIC CAPACITOR FORMING DIELECTRIC OXIDE
FILM METAL FOIL FORMING POLYMER FILM PYRIDINE SOLUTION FORMING ELECTROCONDUCTING POLYMER FILM

DERWENT-CLASS: A26 A85 L03 V01

CPI-CODES: A08-M09A; A09-A03; A10-B; A10-D06; A11-B05A; A11-B05C; A12-E07B; L03-B03A;

EPI-CODES: V01-B01G1; V01-B01G3; V01-B01G8A;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0270U; 0278U ; 0554U ; 0667U ; 0760U ; 0916U
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ENHANCED-POLYMER-INDEXING:
Polymer Index [1.1]
017 ; R00894 G1650 G1649 D01 D23 D22 D31 D41 D51 D54 D56 D59 D84 F08 F07 ; H0000 ; P1412 ; L9999 L2573 L2506 ; L9999 L2540 L2506 ; L9999 L2437*R ; S9999 S1627 S1605 ; S9999 S1616 S1605
Polymer Index [1.2]
017 ; R00898 G2006 D01 D23 D22 D31 D43 D51 D54 D56 D59 D84 F00 ; H0000 ; P1503 ; L9999 L2573 L2506 ; L9999 L2540 L2506 ; L9999 L2437*R ; S9999 S1627 S1605 ; S9999 S1616 S1605
Polymer Index [1.3]
017 ; R00896 G1592 D01 D23 D22 D31 D42 D51 D54 D56 D59 D84 F34 ; H0000 ; L9999 L2573 L2506 ; L9999 L2540 L2506 ; L9999 L2437*R ; S9999 S1627 S1605 ; S9999 S1616 S1605
Polymer Index [1.4]
017 ; R00232 G1650 G1649 D01 D19 D18 D31 D50 D86 F08 F07 ; H0000 ; P1127 P1105 H0293 ; L9999 L2573 L2506 ; L9999 L2540 L2506 ; L9999 L2437*R ; S9999 S1627 S1605 ; S9999 S1616 S1605
Polymer Index [1.5]
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(54) MANUFACTURE OF SOLID-STATE ELECTROLYTIC CAPACITOR

(57)Abstract:

PURPOSE: To enable a solid-state electrolytic capacitor where conductive high- molecular material is used to be lessened in equivalent series resistance and improved in impedance characteristics.

CONSTITUTION: A dielectric oxide film is formed on a valve-action metal foil, then a chemical oxidation polymer film is formed by chemical polymerization, and the valve-action metal foil is dipped into electrolytic polymerizing solution to form an electrolytic polymer film of conductive high molecular material on the chemical oxidation polymer film by electrolytic polymerization. At this point, chemical compound possessed of pyridine rings is added to monomer water solution or oxidizing agent water solution used for chemical polymerization.

LEGAL STATUS

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[Date of extinction of right]

CLAIMS

[Claim(s)]

[Claim 1] After forming a derivative oxide layer in valve action metal foil, a chemical-oxidation-polymerization film is formed by chemistry polymerization. Subsequently, it sets to the manufacture method of the solid electrolytic capacitor which forms the electrolytic polymerization film which immerses into electrolytic polymerization liquid and comes from a conductive polymer substance on an anabolism study oxidation-polymerization film by electrolytic polymerization. The manufacture method of the solid electrolytic capacitor characterized by adding the compound which has a pyridine ring in the monomer aqueous solution used for the above-mentioned chemistry polymerization, or an oxidizing agent solution.

[Claim 2] The manufacture method of the solid electrolytic capacitor according to claim 1 characterized by the loadings of a compound which has the above-mentioned pyridine ring to the above-mentioned monomer aqueous solution being 0.5-5 in a molar ratio to pyrrole 10

[Claim 3] It is the manufacture method of the solid electrolytic capacitor according to claim 1 characterized by the loadings of a compound which has the above-mentioned pyridine ring to the above-mentioned oxidizing agent solution being 0.1 - 5.0wt%.

[Claim 4] It is the manufacture method of the solid electrolytic capacitor according to claim 1 characterized by containing pyridazine, 2-(3-pyridyl) pyrrole, 2, and 3'-bipyridine other than pyridine as a compound which has the above-mentioned pyridine ring.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Concerning the manufacture method of a solid electrolytic capacitor in more detail, this invention relates to the manufacture method of the solid electrolytic capacitor

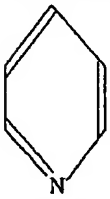
equipped with the solid electrolyte which consists of a conductive polymer substance.
[0002]
[Description of the Prior Art] In order to form in valve action metal foil a conductive polymer substance, for example, the solid electrolyte which consists of polypyrrole, 2 of a chemistry polymerization process and an electrolytic polymerization process processes are carried out.
[0003] Among these, in a chemistry polymerization process, for example, the aluminium etched foil as valve action metal foil with which the derivative oxide layer was formed first is immersed into the aqueous solution containing a pyrrole monomer. Subsequently, it is immersed into the aqueous solution containing oxidizing agents, such as ammonium persulfate, and supporting electrolytes, such as Para toluenesulfonic acid ammonium salt. And it washes and dries, and he usually repeats this 2 to 3 times, and is trying to form a chemical-oxidation-polymerization film on a derivative oxide layer.
[0004] On the other hand, while being immersed into the electrolytic polymerization liquid which consists of a pyrrole monomer, a supporting electrolyte, and a solvent in an electrolytic polymerization process and contacting the anode side electric supply terminal on the chemical-oxidation-polymerization film, electrolytic polymerization is performed with predetermined current density by using the electrolytic polymerization tub side as a cathode. Thereby, the electrolytic polymerization film which consists of polypyrrole is formed on an anabolism study oxidation-polymerization film.
[0005]
[Problem to be solved by the invention] Although a chemical-oxidation-polymerization film and an electrolytic polymerization film are formed as mentioned above, the specific resistance is 1ohm and cm grade, and a chemical-oxidation-polymerization film has it. [quite higher than the specific resistance value of an electrolytic polymerization film] For this reason, the limit was shown also in aiming at the fall of ESR (equivalent series resistance) of the capacitor itself, and an improvement of an impedance characteristic.
[0006]
[Means for solving problem] This invention was made in view of the above-mentioned conventional situation, and [the constitutional feature] After forming a derivative oxide layer in valve action metal foil, a chemical-oxidation-polymerization film is formed by chemistry polymerization. Subsequently, it sets to the manufacture method of the solid electrolytic capacitor which forms the electrolytic polymerization film which immerses into electrolytic polymerization liquid and comes from a conductive polymer substance on an anabolism study oxidation-polymerization film by electrolytic polymerization. It is in adding the compound which has a pyridine ring in the monomer aqueous solution used for the above-mentioned chemistry polymerization, or an oxidizing agent solution.
[0007] That is, in a chemistry polymerization process, valve action metal foil, for example,

aluminium etched foil, is first immersed in the aqueous solution containing a monomer and a solvent, and a monomer is introduced in the pore of this aluminium etched foil. As monomer liquid, the water and the mixed water solution of ethanol which contain 20 - 40wt% of pyrrole preferably are used 5 - 50wt%, for example. Subsequently, although it is immersed in the aqueous solution containing an oxidizing agent and a supporting electrolyte and the monomer in this aluminium etched foil surface and a pore is polymerized in a conductive polymer, in this invention, it is characterized by adding the compound which has a pyridine ring in a monomer aqueous solution or an oxidizing agent solution.

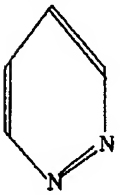
[0008] In this case, if the compound which has a pyridine ring to a monomer aqueous solution is added, as for that loadings, it is desirable that it is 0.5-5 in a molar ratio to pyrrole 10. The effect of an additive is not expected for this loadings to be less than 0.5, and if 5 is exceeded, electric conductivity will fall.

[0009] On the other hand, when adding the compound which has a pyridine ring in an oxidizing agent solution, as for the loadings, it is desirable that it is 0.1 - 5.0wt%. If the effect of an additive is no longer expected like the above for this loadings to be less than 0.1 and 5.0wt% is exceeded, electric conductivity will fall.

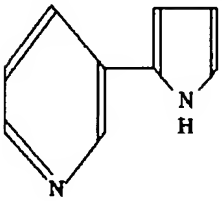
[0010] As a compound which it has, a pyridine ring In addition, [Chemical formula 1]



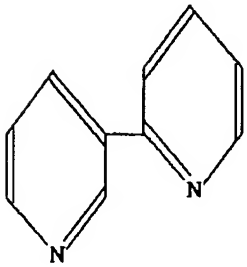
Besides the pyridine shown [Chemical formula 2]



Pyridazine, [Chemical formula 3] which are come out of and shown



2-(3-pyridyl) pyrrole come out of and shown, [Chemical formula 4]



It comes out and the 2 and 3'-bipyridine shown is contained.

[0011] On the other hand, electrolytic polymerization liquid consists of a monomer, a supporting electrolyte, and a solvent. As for the concentration of a monomer, 0.01-5.0mol/l. l. is preferably good in 0.05-3.0mol /. As for the concentration of a supporting electrolyte, 0.01-5.0mol/l. l. is preferably good in 0.05-3.0mol /.

[0012] As a monomer, heterocyclic compounds, such as pyrrole, CHIOFEN, Fran, and aniline, are used.

[0013] As an oxidizing agent, halogen, such as iodine, bromine, and iodination bromine, 5 arsenic fluoride, 5 antimony fluoride, silicon tetrafluoride, phosphorus pentachloride, phosphorus pentafluoride, Metallic halides, such as aluminium chloride and a molybdenum chloride, sulfuric acid, Proton acid, such as nitric acid, fluosulfonic acid, trifluoromethane sulfuric acid, and chlorosulfuric acid, Copper compounds, such as iron compounds, such as peroxide, such as persulfate, such as oxygenated compounds, such as sulfur trioxide and nitrogen dioxide, and ammonium persulfate, hydrogen peroxide, peracetic acid, and difluoro sulfonyl peroxide, ferric nitrate, and ferric sulfate, the 2nd copper of nitric acid, and copper sulfate, etc. are used.

[0014] To a supporting electrolyte, moreover, P-toluenesulfonic acid, naphthalene sulfonic acid, It is independent, or boric acid, such as phosphoric acid, such as carboxylic acid, such as sulfonic acid, such as benzenesulfonic acid, benzoic acid, adipic acid, oxalic acid, and phthalic acid, phenyl phosphoric acid, and naphthyl phosphoric acid, and phenyl boric acid, is mixed, and is used.

[0015] As a solvent, it is independent, or protic solvents, such as ethanol besides water and methanol, and aprotic solvents, such as acetonitrile, propylene carbo NEITO, and N, N dimethylformamide, are mixed, and are used. The kind of solvent is suitably chosen with a supporting electrolyte.

[0016] As valve action metal foil used, 20-300-micrometer thin foil, such as an aluminium, a tantalum, titanium, or niobium, is desirable.

[0017]

[Function] As mentioned above, the small chemical-oxidation-polymerization film of specific resistance is obtained by adding the compound which has a pyridine ring in the monomer aqueous solution used for a chemistry polymerization, or an oxidizing agent solution.

[0018]
[Working example] First, the chemical-oxidation-polymerization film was formed as a simple substance, and the specific resistance rho (ohm-cm) was measured.
[0019] <Comparative example 1> To a 6mol [/l.] (liter) pyrrole monomer aqueous solution, as an oxidizing agent 0.3mol/l. persulfuric acid Amon, When 0.1mol/l. toluenesulfonic acid ammonium salt was mixed, the generated fine particles were fabricated on the pellet with 10mm [in diameter], and a thickness of 1mm and the specific resistance rho was measured by the quadrupole measuring method, they were 1.26 ohm-cm.
[0020] <<Example 1>> After adding pyridine by a molar ratio 10:1 to a 6mol [/l.] pyrrole monomer aqueous solution, 0.3mol/l. persulfuric acid Amon and 0.1mol/l. toluenesulfonic acid ammonium salt were mixed as an oxidizing agent to this pyrrole monomer aqueous solution, and the generated fine particles were fabricated on the pellet with 10mm [in diameter], and a thickness of 1mm. And when the specific resistance rho was measured by the quadrupole measuring method, they were 1.04 ohm-cm.
[0021] <<Example 2>> After adding pyridine by a molar ratio 10:2 to a 6mol [/l.] pyrrole monomer aqueous solution, 0.3mol/l. persulfuric acid Amon and 0.1mol/l. toluenesulfonic acid ammonium salt were mixed as an oxidizing agent to this pyrrole monomer aqueous solution, and the generated fine particles were fabricated on the pellet with 10mm [in diameter], and a thickness of 1mm. And when the specific resistance rho was measured by the quadrupole measuring method, they were 0.21 ohm-cm.
[0022] <<an example 3>> -- in mixing the oxidizing agent solution containing 0.3mol/l. persulfuric acid Amon and 0.1mol/l. toluenesulfonic acid ammonium salt to a 6mol [/l.] pyrrole monomer aqueous solution -- this oxidizing agent solution -- pyridine -- 0.1wt% -- it added. And when the generated fine particles were fabricated on the pellet with 10mm [in diameter], and a thickness of 1mm and the specific resistance rho was measured by the quadrupole measuring method, they were 0.10 ohm-cm.
[0023] <<an example 4>> -- in mixing the oxidizing agent solution containing 0.3mol/l. persulfuric acid Amon and 0.1mol/l. toluenesulfonic acid ammonium salt to a 6mol [/l.] pyrrole monomer aqueous solution -- this oxidizing agent solution -- pyridine -- 0.4wt% -- it added. And when the generated fine particles were fabricated on the pellet with 10mm [in diameter], and a thickness of 1mm and the specific resistance rho was measured by the quadrupole measuring method, they were 0.13 ohm-cm.
[0024] Thus, the small chemical-oxidation-polymerization film of specific resistance is obtained by adding pyridine to either a pyrrole monomer aqueous solution or an oxidizing agent solution. By reference, the comparison result of the specific resistance value of the above-mentioned comparative example 1 and an example 1-4 is shown in Table 1.
[0025]

[Table 1]

	比抵抗ρ（Ω c m）
比較例 1	1．26
実施例 1	1．04
実施例 2	0．21
実施例 3	0．10
実施例 4	0．13

[0026] Next, the solid electrolytic capacitor by polypyrrole of rated 10V3.3micro F was manufactured, and the tangent (tandelta) of electrostatic capacitance (micro F) and a loss angle, and 100kHz o'clock of equivalent series resistance (ESR;momega) were measured.
[0027] <Comparative example 2> The aluminium etched foil (90-100 micrometers in thickness) of 3mm x a 3mm angle was anodized in 33V, and the derivative oxide film was formed in the surface. And after this aluminum foil is immersed in a 6mol/l. pyrrole monomer aqueous solution, Into the oxidizing agent solution containing 0.3mol/l. persulfuric acid Amon and 0.1mol/l. toluenesulfonic acid ammonium salt, it was made to immerse, pull up, wash and dry, and the repetition chemical-oxidation-polymerization film was formed for this 3 times.
[0028] adipic acid ammonium -- 3wt% -- the containing formation -- being immersed into liquid -- formation -- voltage 26V -- re--- after being transformed It was immersed into the aqueous solution which contains alkyl naphthalene sulfonic acid as a conductive polymer monomer, and contains a pyrrole monomer in 0.1mol/l. as 0.2mol [l.] /and a supporting electrolyte, electrolytic polymerization was performed with the current density of 5.6mA/square centimeter, and the electrolytic polymerization film was formed on the chemical-oxidation-polymerization film.
[0029] Next, after printing the carbon layer and silver larer as a cathode drawer layer on the electrolytic polymerization film, respectively and attaching to a lead frame, the resin exterior object was formed in the circumference of each capacitor element by the resin mold method, it did in this way, and 20 solid electrolytic capacitors of rated 10V3.3micro F were manufactured.
[0030] When the tangent (tandelta) of electrostatic capacitance (micro F) and a loss angle, and 100kHz o'clock of equivalent series resistance (ESR;momega) were measured about these, as for the tangent of 3.03 micro F and a loss angle, 0.009 and ESR of electrostatic capacitance were [all] 120mohms by the average.
[0031] <<Example 5>> In performing a chemistry polymerization, in this example 5, pyridine was added at a rate of 10:1 to the 6mol/l. pyrrole monomer aqueous solution at the molar ratio. As the same as the above-mentioned comparative example 2, other conditions manufactured 20 solid electrolytic capacitors of rated 10V3.3micro F. When the tangent (tandelta) of

electrostatic capacitance (micro F) and a loss angle, and 100kHz o'clock of equivalent series resistance (ESR;momega) were measured about these, as for the tangent of 2.98 micro F and a loss angle, 0.008 and ESR of electrostatic capacitance were [all] 80mohms by the average.

[0032] <<Example 6>> In performing a chemistry polymerization, in this example 6, pyridine was added at a rate of 10:2 by the molar ratio to the 6mol/l. pyrrole monomer aqueous solution. As the same as the above-mentioned comparative example 2, other conditions manufactured 20 solid electrolytic capacitors of rated 10V3.3micro F. When the tangent (tandelta) of electrostatic capacitance (micro F) and a loss angle, and 100kHz o'clock of equivalent series resistance (ESR;momega) were measured about these, as for the tangent of 3.05 micro F and a loss angle, 0.009 and ESR of electrostatic capacitance were [all] 72mohms by the average.

[0033] <<an example 7>> -- the inside of the oxidizing agent solution which contains 0.3mol/l. persulfuric acid Amon and 0.1mol/l. toluenesulfonic acid ammonium salt in this example 7 in performing a chemistry polymerization -- pyridine -- 0.1wt% -- it added. As the same as the above-mentioned comparative example 2, other conditions manufactured 20 solid electrolytic capacitors of rated 10V3.3micro F. When the tangent (tandelta) of electrostatic capacitance (micro F) and a loss angle, and 100kHz o'clock of equivalent series resistance (ESR;momega) were measured about these, as for the tangent of 3.11 micro F and a loss angle, 0.010 and ESR of electrostatic capacitance were [all] 73mohms by the average.

[0034] <<an example 8>> -- the inside of the oxidizing agent solution which contains 0.3mol/l. persulfuric acid Amon and 0.1mol/l. toluenesulfonic acid ammonium salt in this example 8 in performing a chemistry polymerization -- pyridine -- 0.4wt% -- it added. As the same as the above-mentioned comparative example 2, other conditions manufactured 20 solid electrolytic capacitors of rated 10V3.3micro F. When the tangent (tandelta) of electrostatic capacitance (micro F) and a loss angle, and 100kHz o'clock of equivalent series resistance (ESR;momega) were measured about these, as for the tangent of 3.03 micro F and a loss angle, 0.009 and ESR of electrostatic capacitance were [all] 75mohms by the average.

[0035] By reference, the comparison result of the above-mentioned comparative example 2 and an example 5-8 is shown in Table 2. Moreover, the reliability test by the rated voltage impression for 1200 hours under 60 degrees C and 95% of relative humidity atmosphere was done. The graph which showed the electrostatic capacitance of the result and change of ESR is shown in drawing 1 .

[0036]

[Table 2]

	静電容量 (μF)	損失角の正接 (tanδ)	ESR at 100kHz (mΩ)
比較例2	3.03	0.009	120
実施例5	2.98	0.008	80
実施例6	3.05	0.009	72
実施例7	3.11	0.010	73
実施例8	3.03	0.009	75

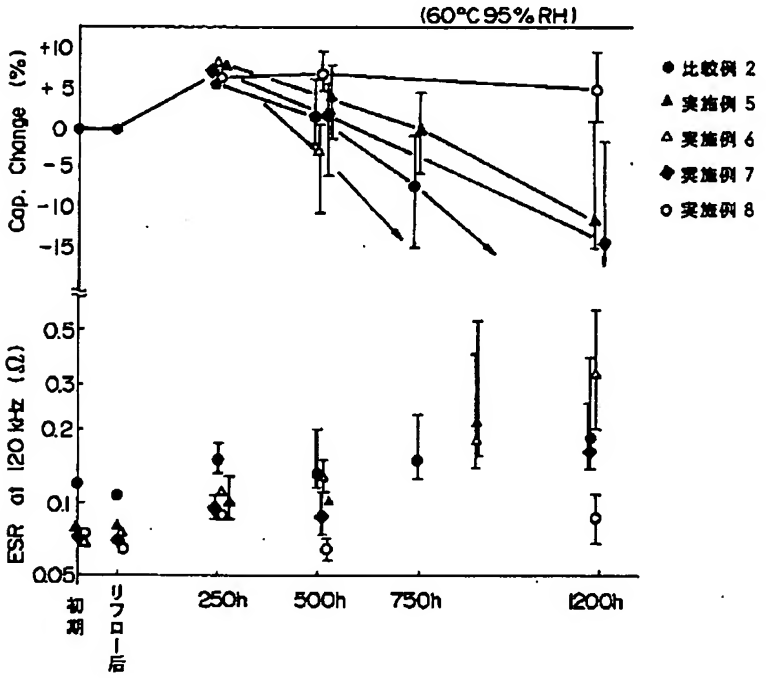
[0037]

[Effect of the Invention] As explained above, according to this invention, specific resistance of a chemical-oxidation-polymerization film can be made small by adding the compound which has a pyridine ring in the monomer aqueous solution used for a chemistry polymerization, or an oxidizing agent solution.

[0038] Therefore, the fall of the equivalent series resistance of a solid electrolytic capacitor and the improvement of an impedance characteristic using a conductive polymer substance can be aimed at.

[Translation done.]

Drawing selection drawing 1



[Translation done.]